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THE INFRARED SPECTRUM OF WATER
IN
CARBON TETRACHLORIDE
AND
CARBON DISULFIDE MATRICES

James Robert Paddock

United States Naval Postgraduate School



THESIS

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by

James Robert Paddock

June 1970

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The Infrared Spectrum of Water
in
Carbon Tetrachloride and Carbon Disulfide Matrices

by

James Robert Paddock
Lieutenant (junior grade), United States Navy
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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the
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ABSTRACT

The infrared spectrum of water is obtained using the matrix isolation technique. Carbon tetrachloride and carbon disulfide are used as matrix materials and found to be effective although not as effective as the inert gases. The resulting spectra show a peak attributable to the monomeric form of water. The causes of this peak are discussed and compared to the literature. The infrared spectrum of pure ice is also obtained and compared to the literature.

TABLE OF CONTENTS

I.	INTRODUCTION-----	9
II.	BACKGROUND-----	11
	A. THE INFRARED SPECTRUM OF WATER-----	11
	B. THE INFRARED SPECTRUM OF ICE-----	13
	C. THE MATRIX ISOLATION TECHNIQUE-----	16
III.	EXPERIMENTAL PROCEDURE -----	19
IV.	EXPERIMENTAL RESULTS-----	25
V.	CONCLUSIONS-----	31
	BIBLIOGRAPHY-----	41
	INITIAL DISTRIBUTION LIST -----	43
	FORM DD 1473 -----	45

LIST OF TABLES

I.	Summary of Experimental Data-----	27
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LIST OF DRAWINGS

1.	Normal Modes of Vibration for the Water Molecule-----	11
2.	Infrared Spectrum of Ice -----	28
3.	Infrared Spectra of Water in Carbon Tetrachloride Matrices -----	29
4.	Infrared Spectra of Water in Carbon Disulfide Matrices-----	30

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I. INTRODUCTION

In studying the internal and intermolecular motions of water, infrared spectroscopy has proven to be an invaluable tool. Since the latter part of the 1800's the infrared spectra of liquid water, water vapor, and ice have been studied extensively. The main reasons for the sustained interest are that water is a most available commodity, it absorbs strongly in the infrared spectral region, and that the questions which have arisen from the study of water have not been completely or satisfactorily answered.

One area that has intrigued many spectroscopists in the study of water is that of the non-hydrogen bonded water molecule. In the vapor phase, virtually no hydrogen bonding is present but in the liquid phase and in ice the forces resulting from hydrogen bonding are considerable. In order to observe the non-hydrogen bonded form of water, or the monomeric form as it is sometimes referred, in the liquid or ice phase requires special spectroscopic techniques. In the liquid phase it was found that OH containing compounds, including water, could be diluted in a non-polar solvent, such as carbon tetrachloride or carbon disulfide, to cause a shift to a higher frequency of the absorption band of the OH containing compound [1-3]. This band was then assigned to the non-hydrogen bonded form of the compound. Borst, et.al. [4] and Fox and Martin [5] were the first

ones to study water in carbon tetrachloride and obtain absorption peaks attributable to the monomeric form of water. Studies similar to these have been performed in this laboratory by Reisinger [6] and Morris [7].

Observation of the monomeric form of water in the ice phase was made possible by the matrix isolation technique first reported by Whittle, et.al. [8]. Basically this technique traps the water molecule in a matrix of inert material which is usually an inert gas or a substance which does not react with the species under study. This matrix is then examined with an infrared spectrometer.

The purpose of the study being reported was to combine the work with non-polar solvents done previously in this laboratory with the matrix isolation technique of Whittle, et.al. [8]. The results obtained showed definite evidence of non-hydrogen bonded water in both carbon tetrachloride and carbon disulfide matrices. This evidence was consistent with similar studies performed using inert gas matrices [8-11].

II. BACKGROUND

A. THE INFRARED SPECTRUM OF WATER

The water molecule is a planar asymmetric top molecule having C_{2V} symmetry. It has three normal modes of vibration, as shown in Figure 1, consisting of two stretching frequencies, ν_1 and ν_3 , and a bending frequency, ν_2 . The symmetric and antisymmetric stretching frequencies, ν_1 and ν_3 respectively, are of approximately the same magnitude while the bending frequency is of much smaller magnitude.

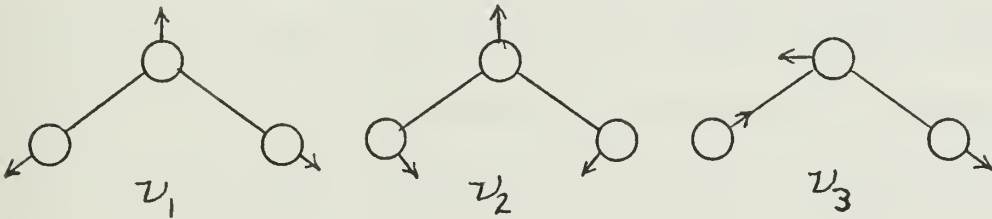


Figure 1. Normal Modes of Vibration for the Water Molecule

The positions and shapes of the characteristic frequencies depend on the environment in which the water molecule is studied. In the vapor phase, the spectrum is basically one of individual water molecules and its sharp peaks for the fundamental modes indicate very little molecular interaction. Benedict, et. al. [12] has done a very extensive study of the infrared spectrum of water and lists the fundamental water vapor vibrational frequencies as: $\nu_1=3657 \text{ cm}^{-1}$,

$\nu_2=1595\text{ cm}^{-1}$, and $\nu_3=3756\text{ cm}^{-1}$ to the nearest reciprocal centimeter.

In the liquid phase, water does not exist as individual molecules but rather as an associated species held together by hydrogen bonding. Because of this hydrogen bonding, the stretching frequencies are coupled to other molecules and exhibit a very broad, intense infrared absorption rather than two sharp peaks as in the vapor phase. This broad band is centered around 3490 cm^{-1} and the bending frequency is centered at 1645 cm^{-1} [13].

In order to eliminate the hydrogen bonding in the liquid phase, Borst, et. al. [4] studied dilute solutions of water in carbon tetrachloride. He reported two absorptions in the stretching region of 3702 and 3611 cm^{-1} . Fox and Martin [5], Reisinger [6], and Morris [7] have confirmed these frequencies at 3705 cm^{-1} and 3614 cm^{-1} . However, none of the workers mentioned was able to observe the bending region of water because the solvent, carbon tetrachloride, absorbed too strongly in this region.

Moving on to the ice phase, as one might expect, the hydrogen bonding forces increase and the stretching frequencies decrease even further than in the liquid phase. Again a broad OH stretching band is observed, this time centered around 3220 cm^{-1} [13]. The bending frequency of ice appears at 1650 cm^{-1} [13] which is very close to that in the liquid phase. This closeness can be explained by two offsetting effects. First of all, the formation of hydrogen bonds tends to

increase the bending frequency slightly [14]. Second, the temperature dependence tends to shift the absorption band to a lower frequency. Thus, these effects tend to offset each other and produce only a small shift from that in the liquid phase.

Eliminating the hydrogen bonding in ice was accomplished by the matrix isolation technique as mentioned earlier. This technique will be examined more closely once the infrared spectrum of ice has been studied in more detail.

B. THE INFRARED SPECTRUM OF ICE

As reported by Ockman [15], ice was one of the first substances to be studied using infrared spectroscopy. The first transmission studies on ice films were performed as early as 1899 by F. A. Saunders of Johns Hopkins University. Since then, the work done in studying ice by infrared techniques has been thorough to say the least. Out of this study, three common forms of ice have been identified: hexagonal ice, cubic ice, and vitreous or glassy ice [16]. In addition to these forms of common ice, there are at least eight other polymorphic forms of ice that are stable at high pressures [13]. All of these forms of ice have been studied extensively in the frequency range 4000 to 30 cm^{-1} by J. E. Bertie, E. Whalley, and co-workers [16-23].

Despite a great deal of work that has been done on the crystal structure of ice and the relative positions of the individual molecules, the vibrational spectrum of ice is difficult to explain because the normal modes of vibration for the ice crystal are unknown [13]. Thus,

each absorption band cannot be definitely assigned to a particular atomic motion as was done in the vapor phase.

The explanation of differences in the infrared spectrum of water vapor and ice lies in the fact that the potential energy changes are different for the two phases. This aspect of the infrared study of ice is treated quite well by Eisenberg and Kauzmann [13] and is summarized here to aid in the understanding of the work done in this report.

The potential energy of an ice crystal U , can be written in the form [24, 25]:

$$U = \sum_j (U_j^0 + U_j^1) + \sum_j \sum_k (U_{jk} + U_{Lj}) + U_L \quad (1)$$

Here the U_j^0 term is the potential associated with the isolated j^{th} molecule and the remaining terms all have to do with the perturbations caused by neighboring molecules.

The U_j^1 term describes what is known as the static field effect. This is the change that results in U_j^0 due to the neighboring molecules fixed in their equilibrium positions. Thus, U_j^1 accounts for the shifts in absorption peaks due to electrostatic forces, hydrogen bonding, and other forces that would act on the molecule if all of the neighboring molecules were held motionless. As expected, in ice, hydrogen bonding accounts for most of the static field effects.

The term U_L arises from vibrations of the lattice and as such is a function of the location and orientation of the neighboring molecules.

A lattice mode can consist of a hindered translation, a hindered rotation called a libration, or some combination of the two. Generally these type of vibrations occur at rather low frequencies.

The coupling of the intramolecular modes of the j^{th} and k^{th} molecules result in the U_{jk} term. This differs from U_j^0 in that it depends on displacements of the atoms in both the j^{th} and k^{th} molecules. This effect tends to complicate a molecule's spectrum but can be circumvented by various isotopic substitutions that will not be discussed here. The final term, U_{Lj} , describes the coupling of lattice vibrations with intramolecular displacements. This effect is quite small in ice and will not be considered further.

Using Equation 1 it is possible to qualitatively describe the spectrum of ice as compared to that of water vapor. The fact that only one broad band occurs is due to the U_{jk} term. That is, the ν_1 and ν_3 frequencies of one molecule couple with the ν_1 and ν_3 frequencies of the neighboring molecules and produce a broad absorption peak. The fact that this peak is centered at a lower frequency is due to the static field term, U_j^1 , which is comprised mostly of hydrogen bonding [14]. Hydrogen bonding also appears to be partly responsible for the broad absorption band associated with the stretching frequencies [13]. This is because the U_j^1 term varies from molecule to molecule depending upon the individual environment. Hence, the stretching frequencies will also vary and the absorption band is spread out.

The broad absorption peak in the stretching frequency region is

characteristic of all the ice polymorphs. In fact, all the spectra of ice are quite similar to hexagonal ice, ice I, at all frequencies.

Hornig, et.al. [26] and Bertie and Whalley [18] found that the infra-red spectra of cubic ice and ice I were virtually identical. This is because their nearest neighbors are the same and, hence, their U_j^i and U_{jk} terms in Equation 1 will be almost the same. Thus, the only terms that will differ will be due to the minor term U_{Lj} .

By examining Equation 1 closely, it is apparent that elimination of the terms resulting from nearest neighbor interactions would produce a potential similar to that experienced in the vapor phase. The technique used to accomplish this feat was the matrix isolation technique.

C. THE MATRIX ISOLATION TECHNIQUE

The intent of the matrix isolation technique is to trap an active material in an inert matrix at a low enough temperature to prevent diffusion of the active species and thus holding it in an unreactive environment [8]. It should be kept in mind that an active species may only be a molecule capable of forming hydrogen bonds, it may be a free radical, or it could be any substance that is difficult to observe using ordinary spectroscopic techniques due to its high reactivity.

The desirable properties of a matrix are listed by Becker and Pimental [9] as follows: (a) Inertness - The matrix material must be inert with respect to reaction with the active species. In this

respect the rare gases are ideal although by no means necessary.

(b) Rigidity - A matrix must be sufficiently rigid to prevent diffusion of the active species. The matrix must also be suitable for placing the active species either in a lattice position or in a lattice opening. Because of these requirements, the suitability of a given matrix is highly temperature dependent. (c) Transparency - Obviously the matrix must be able to transmit light to be effective but it must have no absorption bands in the spectral region of interest as well. Even a weak absorbance will appear significant at high mole ratios of matrix material to active species. Besides being non-absorbing, the matrix should not scatter the incident light to any great extent. Experimentation by Becker and Pimental [9] has shown that a glassy matrix rather than a crystalline one best satisfies this criterion. This effect is also highly temperature dependent. (d) Volatility - The vapor pressure of the matrix is very important. It must be high enough at room temperature to enable easy mixing with the active species but it must have a low enough vapor pressure at the low temperature and high vacuum conditions, under which the matrix is studied, to remain rigid. Obviously this requirement is also highly temperature dependent and, in fact, tends to place an upper limit on the temperature range at which a matrix can still be effective. (e) Mole ratio - In addition to the above requirements, the mole ratio of matrix material to active species must be as high as possible. The effective ratio

will vary from matrix to matrix depending on the crystal structure and temperature but generally it must be greater than 100 to 1 to minimize the statistical probability of two active species molecules occupying neighboring positions in the matrix.

Results of studies using the matrix isolation technique on hydrogen bonded species correlate quite well with those of the vapor phase. The correlation is not perfect, however, due to a difference in the dielectric constant in the matrix compared to that of the vapor [9].

III. EXPERIMENTAL PROCEDURE

All spectra were recorded on a Perkin - Elmer Model 621 Grating Infrared Spectrophotometer used in the double beam mode of operation. The instrument was calibrated using the 0.05 mm polyethylene standard window provided with the instrument and the critical frequencies checked out as published.

The sample cell used was of special design to meet the conditions necessary for a matrix isolation study. It consisted of a 7/8 inch diameter cesium bromide disc in thermal contact with a copper holder. This holder was then connected to a dewar vacuum by a copper house-keeper seal. At the bottom of the dewar vacuum was a cavity in which the cesium bromide disc could be rotated. In one position the disc was aligned with a side arm through which the sample was sprayed onto the disc. In the other position, the disc was rotated 90° from the previous position and was aligned with two 1-1/2 inch diameter cesium bromide plates at either end of the vacuum cavity. Aligning the disc in either of these positions was accomplished by turning about a 55/50 ground glass joint through which the dewar with the connected disc was attached to the bottom cavity.

Most of the spectra that were run used the recommended control settings for a detailed survey analysis. There were a few spectra that were taken using improved resolution techniques and these were

done using the recommended control settings for a 5X ordinate expansion. Throughout all spectral runs, the spectrometer was purged using dry air as recommended in the operating manual. Despite this precaution to eliminate atmospheric water vapor and carbon dioxide, some water vapor rotational peaks were evident under improved resolution operating conditions.

The carbon tetrachloride used in the experiment was Mallinckrodt Chemical Works spectrophotometric grade reagent. No other purification was necessary. However, before using the carbon tetrachloride as a matrix material, it was used to purge the system of absorbed water in the system. This procedure was analogous to, but much easier than, the drying process used previously in this laboratory [6, 7, 27]. The water was eliminated from the system when the carbon tetrachloride was placed on a standard vacuum system and allowed to diffuse into the system without any pumping. The carbon tetrachloride container was then closed and the system pumped clear. This process was repeated three or four times which was found to be sufficient to eliminate any absorption due to water in an infrared analysis of thin films of carbon tetrachloride.

The carbon disulfide that was used was Fisher Scientific Company grade reagent. No further purification was performed, although the system was purged in the same manner as for carbon tetrachloride with the same results. The water used in all cases was recently distilled water.

All of the sample preparation was performed on a standard vacuum system capable of maintaining a pressure of about 10^{-3} torr. Both the carbon tetrachloride and carbon disulfide reagents were kept in glass sample holders about 12 mm inside diameter and approximately 12 inches long with viton o-ring stopcocks controlling the opening to the vacuum system. The special stopcocks were deemed necessary to prevent the reaction of the carbon tetrachloride or carbon disulfide with the stopcock grease. The water was kept in a similar glass sample holder but with a standard stopcock.

Sample preparation began by mixing a certain amount of water vapor with the desired amount of matrix material (carbon tetrachloride or carbon disulfide). This preparation was accomplished in the following manner: A certain amount of water vapor was allowed to diffuse into the vacuum system and an attached mixing vessel. The amount was measured on a mercury manometer capable of measuring the vapor pressure to one torr. While the water vapor was in the system, the matrix material was added until the manometer gave the total vapor pressure required for the desired sample ratio. Since the water vapor and matrix material could not be added to the mixing vessel separately, a small error was introduced into the mole ratio when the mixing vessel was closed off and the system evacuated. This was brought about because the matrix material, having a much higher vapor pressure than water, was forcing the water into the mixing vessel. Thus, when the vessel was closed off, the mixture remaining

was virtually pure matrix vapor and the sample in the mixing vessel was not in the same proportions as measured on the mercury manometer. By making the mixing vessel much larger in volume than the system tubing, the mole ratio error was minimized to about two per cent.

Once the water vapor and matrix material were in the mixing vessel, they were allowed to mix as gases. Whenever possible the sample was allowed to mix overnight or longer. When this was not convenient, a special paddle wheel arrangement, capable of being turned by a magnetic stirrer, was used. Becker and Pimental [9] used another technique which involved introducing the sample into a bulb with teflon chips and physically shaking the bulb to insure a homogeneous mixture. It was felt that the methods mentioned above were equal in their ability to provide a homogeneous mixture. Thus, none of the three methods was preferred over any of the other methods.

Once the sample was mixed, the sample cell was placed on the vacuum system and evacuated. When a pressure of less than 10^{-3} torr was obtained, liquid nitrogen (b. p. 77°K) was placed in the dewar connected to the cesium bromide disc. The disc was then allowed to cool for twenty minutes. It was found that cooling much longer than this caused the stopcock grease on the 55/50 ground glass joint to freeze and made alignment with the other two cesium bromide discs almost impossible. When the disc had cooled sufficiently, the sample was allowed to flow from the mixing vessel onto the disc. The cesium

bromide plates were then aligned and the sample cell was placed in the spectrometer. The reference beam was then adjusted using a reference beam attenuator to give an initial transmittance reading of about eighty per cent.

No attempt was made to measure the sample thickness. The sample thickness was maintained as constant as possible, however, over the various runs by diffusing the same amount of sample, as measured on the mercury manometer, onto the cesium bromide disc. Similarly, the temperature of the cesium bromide disc was not measured absolutely, rather, it was held constant by cooling with liquid nitrogen the same length of time for each sample. By comparing the spectrum of a pure ice film under the same conditions as those of the matrix samples with the ice film spectra reported by Bertie, et. al. [18,23], a disc temperature of approximately 120°K was estimated from his data.

With the temperature and sample thickness, as well as the other ambient conditions, being held as constant as possible, spectra were obtained for all samples in the stretching and bending regions of water. The only quantity that was varied was the mole ratio of matrix material to water vapor. These ratios varied from 1:2 to 13:1 for both carbon tetrachloride and carbon disulfide. In addition to these spectra, runs were made on pure water, carbon tetrachloride, and carbon disulfide.

The spectra of all of the samples were recorded as a plot of percent transmittance versus frequency in reciprocal centimeters. When

needed, spectra were converted to a plot of absorbance versus frequency by using a Hewlett - Packard Calculator - Plotter Model 9100A. This conversion was easily accomplished using data from the original transmittance plot and a simple calculator program for calculating absorbance from percent transmittance.

IV. EXPERIMENTAL RESULTS

The main results of this study are contained in Table I. Here the variations caused by the mole ratio of matrix material to water variation can be seen as well as the differences between carbon tetrachloride and carbon disulfide. From the table it is apparent that most of the variations are located in the OH stretching region of water and, hence, this was the main region of interest. For the sake of comparison the OH stretching region of a pure ice film is shown in Figure 2 along with the same region for various carbon tetrachloride matrices in Figure 3 and carbon disulfide matrices in Figure 4. These figures were all obtained by tracing over the original spectra.

In comparing the spectra it is convenient to refer to the peak at 3658 cm^{-1} in carbon tetrachloride and 3628 cm^{-1} in carbon disulfide as Peak A, the broad absorption band around 3300 cm^{-1} as Peak B, and the bending peak as Peak C. From Figures 3 and 4 it appears that as the mole ratio of matrix material to water increases, the absorption due to Peak A relative to Peak B decreases. This is not the case as can be seen in Table I where the absorption of the two bands are in absorbance units rather than percent transmittance units which do not show the logarithmic nature of the absorption.

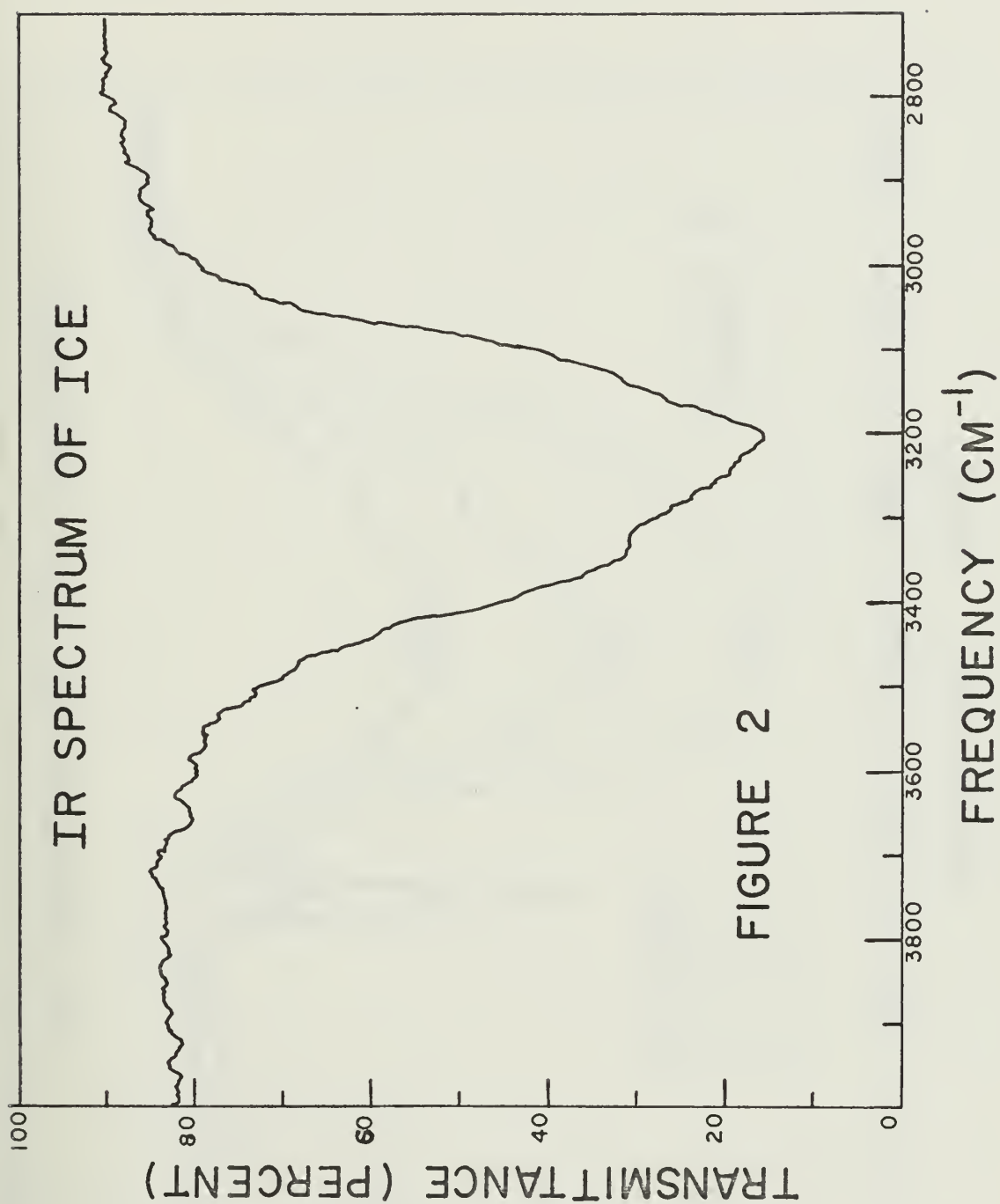
From Table I the following facts are noteworthy: (a) The location of Peak C does not vary in either the carbon tetrachloride matrix or

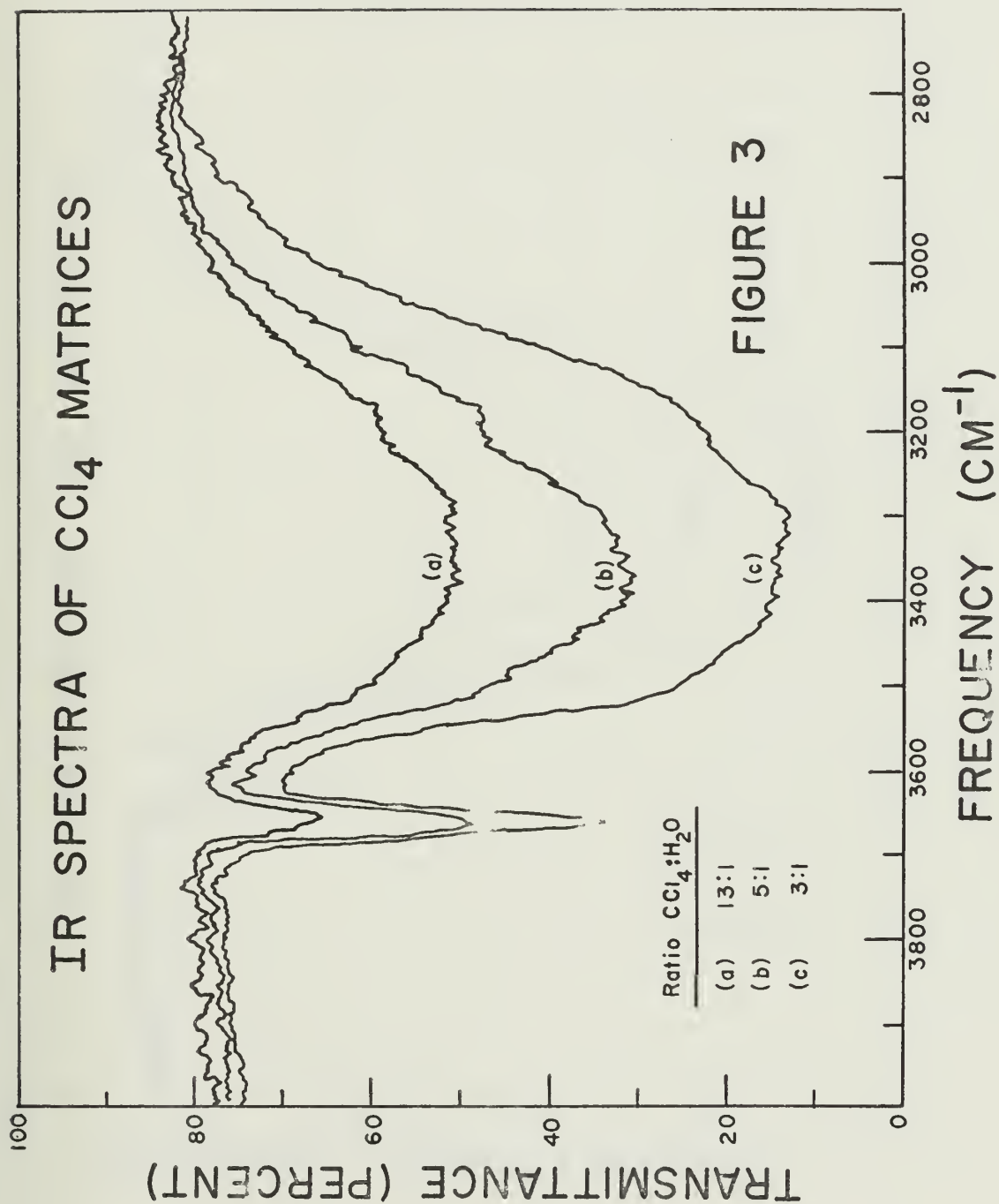
carbon disulfide matrix and does not vary in going from one matrix to the other. (b) The location of Peak A does not vary in either matrix but shifts 30 cm^{-1} in going from the carbon tetrachloride to the carbon disulfide matrix. (c) The location of Peak B shifts significantly in the carbon tetrachloride matrix to a lower frequency as the matrix material to water ratio is increased. A very slight shift of the same nature occurs in the carbon disulfide matrix although the shift could hardly be called significant. In fact, the shift might even be non-existent as the location of the peak cannot be accurately placed much better than within about 10 cm^{-1} . (d) The ratio of Peak A absorbance to Peak B absorbance increases with increasing matrix material to water ratios for both the carbon tetrachloride and carbon disulfide matrices with the one exception of the 13:1 ratio of carbon disulfide to water. This absorbance ratio is much lower, however, for carbon disulfide matrices than for the corresponding carbon tetrachloride matrices. In addition to the above trends noticed in the data of Table 1, it was observed that Peak A increased slightly in bandwidth and became less sharp as the mole ratio of matrix material to water was increased.

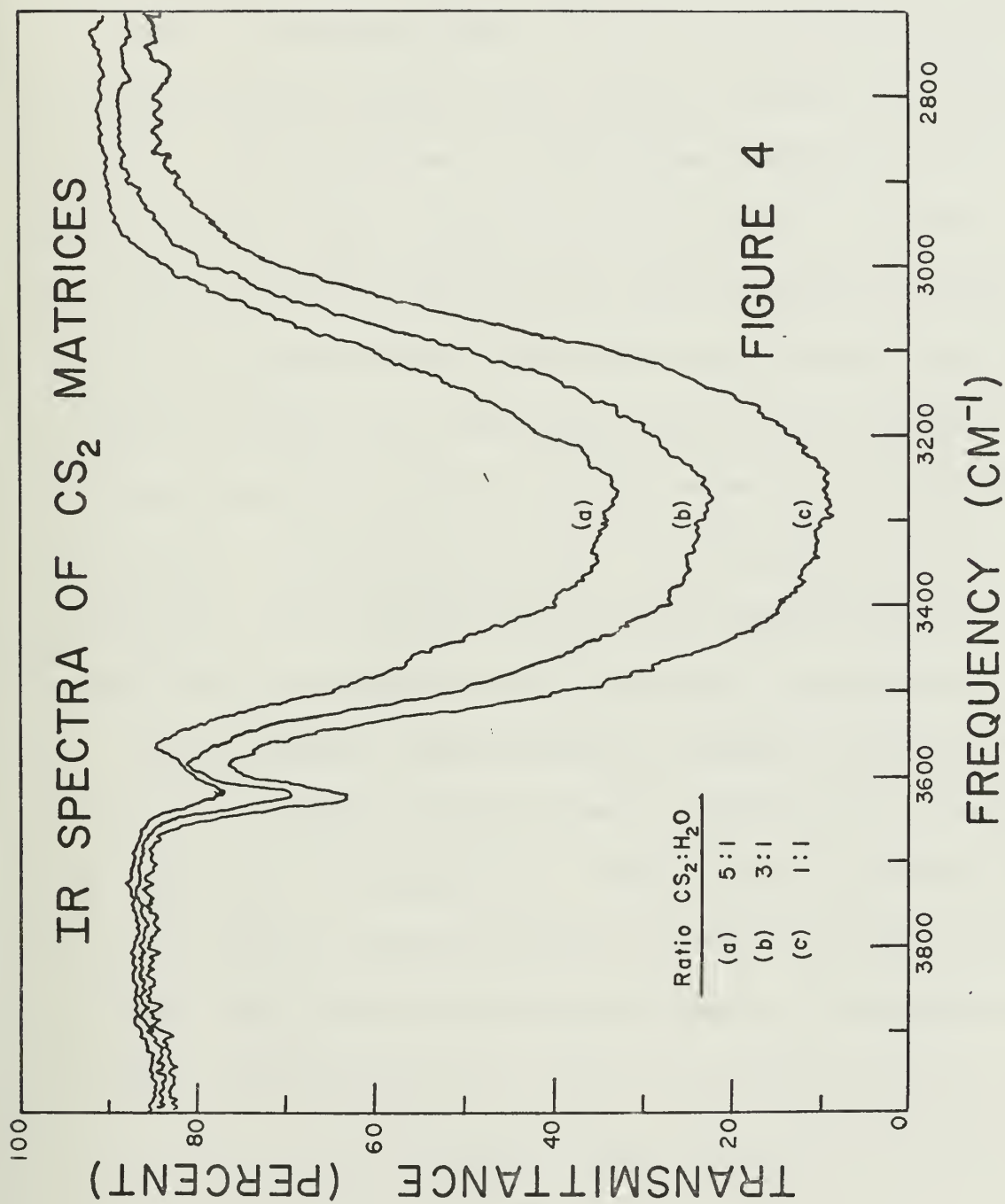
Table I

Ratio $\text{CCl}_4:\text{H}_2\text{O}$	1:2	1:1	2:1	3:1	4:1	5:1	13:1
Base Transmittance (%)	80.0	83.0	77.0	84.0	80.0	83.0	80.5
Peak A (cm^{-1})	3656	3657	3657	3658	3658	3660	3659
A Transmittance (%)	62.0	52.6	44.4	40.4	42.2	50.7	60.1
A Absorbance	.111	.198	.239	.318	.278	.214	.127
Peak B (cm^{-1})	3280	3290	3300	3320	3330	3350	3360
B Transmittance (%)	16.0	13.2	11.5	14.9	21.8	32.5	48.2
B Absorbance	.699	.799	.826	.751	.565	.407	.223
$\frac{\text{A Absorbance}}{\text{B Absorbance}}$.158	.248	.290	.423	.492	.525	.570
Peak C (cm^{-1})	1621	1618	1620	1620	1618	1615	1617

Ratio $\text{CS}_2:\text{H}_2\text{O}$	1:2	1:1	2:1	3:1	4:1	5:1	13:1
Base Transmittance (%)	81.0	82.0	80.0	83.0	83.0	89.0	84.0
Peak A (cm^{-1})	3628	3628	3630	3625	3627	3630	3620
A Transmittance (%)	67.4	60.1	57.8	62.0	65.4	72.1	76.0
A Absorbance	.080	.135	.141	.127	.103	.091	.043
Peak B (cm^{-1})	3280	3280	3280	3280	3290	3290	3300
B Transmittance (%)	14.1	6.1	10.4	15.2	23.6	31.2	49.5
B Absorbance	.759	1.128	.886	.737	.546	.455	.229
$\frac{\text{A Absorbance}}{\text{B Absorbance}}$.105	.120	.159	.172	.189	.201	.189
Peak C (cm^{-1})	1622	1622	1622	1620	1621	1620	1620







V. CONCLUSIONS

Prior to obtaining the spectra of water in carbon tetrachloride or carbon disulfide using the matrix isolation technique, the results of Bertie, et. al. [16,23] were confirmed upon analysis of a pure ice film spectrum. All of the peaks listed by Bertie were observed in this laboratory but with small frequency shifts assumed to be due to a variation in temperature. This variation was estimated to be about 20°K warmer than Bertie's experiment from the shift of both the bending frequency [28] and the stretching frequency [20]. Thus, with the amount of cooling described earlier for this experiment, the temperature of the cesium bromide disc being obtained was probably about 120°K since Bertie's work was performed at approximately 100°K.

Besides enabling a rough temperature estimate, comparison with Bertie's work indicated that the ice being studied in this experiment was either cubic or hexagonal ice. It did not appear important enough to try and determine which of the two ice forms was present, since it has been found by several workers that the spectra of both forms are virtually identical [16,26,29]. This is not surprising since both cubic and hexagonal ice have identical nearest neighbors and thus will have practically the same potential energy function (Equation 1) as mentioned earlier. What is important in knowing the type of ice being formed is that it is not vitreous ice. This form of ice is formed when water vapor condenses on a surface maintained below 110°K. The resulting

structure is of a glassy nature which varies, depending upon its past history [20]. Thus, if vitreous ice had been formed in this experiment, a great deal of variation would have been evident in the resulting spectra. This was not observed. Even if some vitreous ice had been formed, it probably would not have lasted very long. The reason for this is that vitreous ice transforms irreversibly upon warming to cubic ice which, upon continued warming, transforms to hexagonal ice [13]. Thus, even if the cesium bromide disc should have cooled below 110°K allowing vitreous ice to be formed, the infrared radiation of the spectrometer should have warmed the sample enough so that either cubic or hexagonal ice was formed. Again, the consistency of the results indicated that vitreous ice was not a significant problem.

Having confirmed the infrared spectrum of thin ice films, the matrix isolation technique was employed to further study the infrared spectrum of ice. As mentioned earlier, this same type of study has been performed using nitrogen, argon, krypton, and xenon [9, 10, 11] as matrices at much lower temperatures with exceptionally good results. The success of this technique, however, is only as good as the matrix in which the water is studied. Thus, it is pertinent to discuss the matrix characteristics of carbon tetrachloride and carbon disulfide compared to the characteristics of an ideal matrix listed earlier in this paper.

The inertness of the matrix material with respect to the active species is of prime importance. Thus, carbon tetrachloride and

carbon disulfide, because water is slightly soluble in both of them, are only moderately inert as compared to the rare gases or nitrogen. However, compared to many other possible matrix materials, carbon tetrachloride and carbon disulfide are both exceptionally inert. It has been determined that water is soluble in carbon tetrachloride to about 0.010% at 24°C [30] and water is soluble in carbon disulfide to about 0.10% at 25°C [31] or about ten times that in carbon tetrachloride. On this basis, one would expect carbon tetrachloride to be a slightly better matrix material than carbon disulfide since it is less reactive with water.

The second desirable characteristic of a good matrix material, rigidity, is difficult to access in carbon tetrachloride and carbon disulfide. Both species have a reasonably high vapor pressure at room temperatures and a vapor pressure that goes below one millimeter at temperatures considerably higher than the temperatures of this study. Nevertheless, it is not known how much vapor pressure is needed for diffusion of the matrix species to cause loss of rigidity. As a result, both carbon tetrachloride and carbon disulfide might be unsuitable in this regard. The rigidity aspect of the two matrix materials was not checked with respect to the position of the water molecule in the matrix either. That is, whether or not the water molecule actually occupied a position in the lattice or whether it was in a lattice opening was not studied. The fact that the spectra which were studied did not change in appearance after more than two hours

indicates that water was not diffusing through the lattice and, hence, that the matrix was sufficiently rigid for use as a good matrix material. If this were not the case, an increase in the absorbance of the polymeric species and a decrease in the absorbance of the monomeric species would have been noted as the monomeric species diffused close enough to each other to form hydrogen bonds and become polymeric species.

The transparency of carbon tetrachloride and carbon disulfide has long been used by spectroscopists in infrared studies, much to their advantage. Both species are transparent over large regions of the infrared spectrum, most notably, the stretching region of water. The bending region in ice is slightly obscured by the absorption of the two matrix materials but not totally. Thus, the transparency of the two matrix materials did not present any serious problems. The scattering problem exhibited by some matrices was not encountered in this study, most likely due to the matrix being glassy in nature [9].

The final criterion of a good matrix is the mole ratio of matrix material to active species. From the previous matrix isolation studies of water [8-11], the use of a matrix material to water ratio of less than one hundred to one was not considered useful. With both carbon tetrachloride and carbon disulfide, however, acceptable results were obtained using mole ratios varying from 1:2 to 13:1. The literature results, where mole ratios of greater than one hundred to one were obtained, gave significantly better results in the spectra but

were generally similar to those in this study at much lower mole ratios of matrix material to water.

From the spectra of the carbon tetrachloride and carbon disulfide matrices, the peak at 3658 and 3628 cm^{-1} respectively, Peak A, was easily attributable to non-hydrogen bonded water. The fact that only one peak was observed proved to be slightly disconcerting since a symmetric stretching band and an asymmetric stretching band would normally be expected in this region. There are two possible explanations for the single peak. It is possible that the observed peak was due to the asymmetric stretching mode and that the symmetric mode absorbed somewhere in the broad absorption band of Peak B. This is possible if the carbon tetrachloride or carbon disulfide matrix caused a considerable shift from the frequencies reported by Van Thiel, et. al. [10]. In this paper Van Thiel reports an asymmetric stretching frequency of 3725 cm^{-1} and a symmetric stretching frequency of 3627 cm^{-1} . Thus, if Peak A observed in this experiment were due to the asymmetric stretching frequency, then the symmetric stretching frequency would be expected around 3560 cm^{-1} if it shifts as much as the asymmetric stretching frequency. This frequency is located on the high frequency side of Peak B and appears to be a smooth absorbance without any shoulder possibly attributable to the symmetric stretching frequency. This evidence, however, does not rule out the existence of the peak at 3560 cm^{-1} . The peak assigned to the symmetric stretching frequency by Van Thiel [10] was of much less

intensity than the asymmetric stretching frequency. Thus, if this were the case in this study, the peak might have been too weak to have produced a shoulder or perhaps it was too weak to even be observed.

The second possible explanation of Peak A is that it is an unresolved spectrum of the two non-hydrogen bonded water stretching frequencies brought closer together by lattice interactions. This explanation has one apparent drawback in that the absorption band is quite narrow indicating little interaction of the two modes. Generally the band tends to be rather broad when two frequencies are brought together by lattice interactions. On the other hand, the peak location corresponds quite nicely to an average absorption at 3676 cm^{-1} for the two stretching frequencies reported by Van Thiel [10]. Van Thiel also shows his spectra with decreasing matrix material to water mole ratios from 1012:1 to 39:1. By extrapolating the general features of these spectra to the extremely low mole ratios used in this study, a very close correlation is observed with a single peak for Peak A and a very broad single peak for Peak B. Furthermore, at the higher mole ratios of matrix material to water, Peak A appears to show some structure suggesting a doublet rather than a singlet absorption band. This would agree quite well with Van Thiel's results [10].

The appearance of structure in Peak B was minimal in this study indicating that the matrix isolation technique was not as effective as it might have been. Had the technique offered better resolution, the

individual bands contributing to the very broad Peak B might have been observed. With no evident structure, it is impossible to separate the contributing bands without knowing the exact number of peaks involved and their shapes. About the only definite conclusion that can be reached concerning Peak B is that it is comprised of more bands than are found in pure ice. This can be verified by checking Figures 2, 3, and 4. Again comparing the results of this study with that of Van Thiel's [10] shows that there are several peaks absorbing in the region of Peak B. These peaks are assigned to various dimer, trimer, tetramer, and polymer mixture species. If each of these species has at least two stretching frequencies then there are potentially numerous bands capable of being resolved from Peak B. However, neither carbon tetrachloride or carbon disulfide gave the resolution necessary for assigning peaks other than the monomer peak, Peak A. In addition to the many potential bands in Peak B, there is the possibility that the second overtone of the bending frequency occurs in the region of Peak B. Furthermore, this band may couple with a stretching band by Fermi resonance. This is basically a "borrowing" of intensity by one band from a neighboring band of the same symmetry. The frequencies of both bands then are shifted from their normal positions [13]. This effect, as with the coupling of other bands, causes the peak to spread out. Bertie and Whalley [20] do not consider Fermi resonance as a contributing factor in the spreading out of the polymeric stretching band because the ice molecule basically has no

symmetry. Thus, each normal vibration consists of various translational, vibrational, and rotational motions which do not mix with the internal motions of the molecule. As a result no Fermi resonance can exist. Whether or not Fermi resonance exists does not appear significant in the interpretation of Peak B. There are contributing bands in Peak B which are not present in the spectrum of pure ice and which appear to be caused by low polymeric species. Supporting this fact is the shift in maximum absorption as the mole ratio of carbon tetrachloride to water is changed. As the mole ratio was increased the maximum absorption frequency of Peak B was increased also. This is the same trend noted by Van Thiel [10].

The same shift in Peak B is barely noticeable in a carbon disulfide matrix and is most likely due to the difference between the carbon tetrachloride and carbon disulfide matrices. The carbon tetrachloride matrices appear to be more effective than the carbon disulfide matrices. This fact is most evident in the relative absorbance ratio of monomer absorbance to polymer absorbance for the two types of matrix materials. The ratio in carbon tetrachloride is much higher than in carbon disulfide indicating a greater amount of monomeric water being obtained. As mentioned earlier, the fact that water interacts with carbon tetrachloride less than with carbon disulfide probably accounts for the fact that carbon tetrachloride is a better matrix material. However, the reason could also be due to one or more of the other characteristics of a good matrix material.

The interaction with water aspect of the two matrix materials could well account for the position of Peak A. Catalano and Milligan [11] state that the frequency of the OH stretching frequency will shift to lower frequencies if there is any interaction with the matrix. Thus, if Peak A is an average of the two stretching frequencies, the average frequency should decrease in going from Van Thiel's work with nitrogen [10] to carbon tetrachloride to carbon disulfide. This is exactly the trend observed with the average frequencies being 3676, 3658, and 3628 cm^{-1} respectively. It should be noted, however, that the average frequency does not have to be used for comparison. If Peak A were the asymmetric stretching frequency, the order would still be the same. Thus, although the shifts seem to favor Peak A being an average of the two stretching frequencies, the evidence for it being the asymmetric stretching frequency alone is still considerable.

As previously stated, the bending region of water was slightly obscured by the two matrix materials used in this experiment. Because of this most of the study was performed in the stretching region. It was noted, however, that the position of Peak C, the bending frequency, did not change position with changing mole ratios or changing matrix materials. The fact that the bending frequency is virtually unaffected by environmental changes has been reported by Vedder and Hornig [25] previously. Thus, in going from the vapor phase of water, through the liquid phase, to ice, the bending frequency only shifts from 1595, to 1645, to 1650 cm^{-1} respectively [13]. The results obtained in the

bending region, then, tend to confirm the unreactivity of the bending frequency in various environments.

In summary then, the effectiveness of carbon tetrachloride and carbon disulfide as matrix materials in a matrix isolation study, although not as effective as the inert gases, gave good results overall. The spectra obtained showed definite evidence of a non-hydrogen bonded species in a sharp peak, Peak A. This peak was due either to the asymmetric stretching frequency or, more likely, to an average combination of the symmetric and asymmetric stretching frequencies. Finally, the broad absorption band, Peak B showed evidence that low numbered polymeric species caused the absorption band to broaden more than was evident in the spectrum of pure ice.

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Carbon Disulfide						
Matrix						
Absorption						
Water						
Ice						
Interaction						
Frequency						

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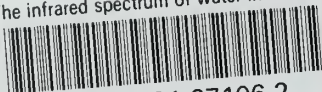
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